^{35}Cl NQR Relaxation of the Molecular Ferroelectric 5,6-Dichloro-2-Methylbenzimidazole with Hydrogen-Bonded Molecular Chain

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Abstract: The ^{35}Cl nuclear quadruple resonance (NQR) frequencies and spin-lattice relaxation times were measured in the temperature range of 4.2–420 K, of the above-room-temperature ferroelectric 5,6-dichloro-2-methylbenzimidazole, the ferroelectricity of which is thought to arise from the positional ordering of protons along chain of N-H...N hydrogen bonds. The first-order phase transition was clearly detected at around 400 K, as a discontinuity in the temperature dependence of NQR frequencies. The two NQR lines observed showed a much more significant difference in frequency in the high-temperature phase. This is consistent with the recently reported symmetry-lowering of crystal structure on warming. The relaxation mechanism in the low-temperature phase is discussed.

1. Introduction

DC-MBI (5,6-Dichloro-2-methylbenzimidazole) has been reported by Horiuchi et al. [1] to exhibit ferroelectricity above room temperature. In the crystal, there exist molecular chain connected by N-H...N hydrogen bonds (Figure 1). The ferroelectricity is thought to arise from the positional ordering of protons along chain of N-H...N hydrogen bonds. Minami et al. performed polarization-retention measurements [2] to observe the dielectric relaxation of spontaneous polarization and found that extracted relaxation time shows a deviation from the classical Arrhenius-type temperature dependence at low temperatures below 100 K [3]. The relaxation was considered to be relating to a ferroelectric domain-wall motion. The non-Arrhenius behavior, in which the relaxation time approaches a constant value of ca. 4×10^{-5} s at low temperatures, may be explained by quantum relaxation as reported for the domain-wall motion in ferromagnetics [4]. If this is the case, the quantum relaxation will be responsible also for the NQR relaxation at low temperatures, since the domain-wall creep by successive quantum tunneling will be accompanied by a local fluctuation of the electric field gradient (EFG). In the present study, it was challenged to detect the domain-wall motion due to quantum tunneling, by NQR spin-lattice relaxation time measurements.
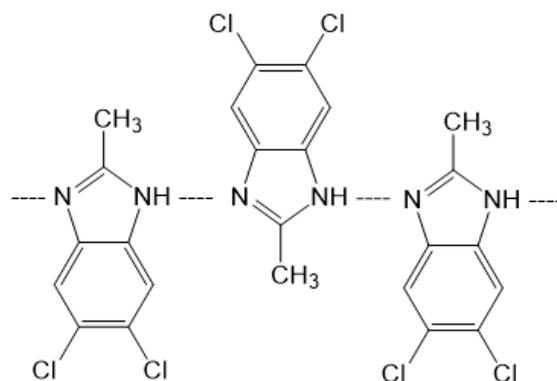
Figure 1. Hydrogen-bonded molecular chain of 5,6-dichloro-2-methylbenzimidazole (DC-MBI).

2. Experimental

The purchased 5,6-dichloro-2-methylbenzimidazole (DC-MBI) was recrystallized by the slow evaporation of the ethanol solution in a vacuum desiccator with NaOH as absorbent. The powder X-ray diffraction measurements were conducted by Rigaku Rint 2100 using Cu Kα radiation (Rigaku Co., Akishima, Tokyo, Japan). ^{35}Cl nuclear quadruple resonance (NQR) measurements were performed using a pulsed spectrometer based on the Matec gated amplifier 525 (Matec Instruments, Inc., Warwick, RI, USA). The spin-lattice relaxation time T_{1Q} was determined by the inversion recovery method. The signal intensity was monitored by the echo height. ^{1}H nuclear magnetic resonance (NMR) spin-lattice relaxation time T_1 was measured by use of a Thamway's spectrometer (PROT3100MR, Thamway Co., Ltd, Fuji, Shizuoka, Japan) at 45.08 MHz by the saturation recovery method using a comb-τ-90°(x)-τ_e-90°(y) pulse sequence.

3. Results and Discussion

The obtained crystals were identified by the powder X-ray diffraction as shown in Figure 2. For the NQR measurements, the frequency ranges of 36.1 ± 1 MHz and 35.7 ± 3 MHz were swept at 77 K and room temperature, respectively. Two ^{35}Cl NQR lines closely separated were observed at 36.0925 MHz and 36.107 MHz at 77 K. Since all molecules in the crystal are crystallographically equivalent [1], these two resonance lines can be assigned to the two chlorine atoms in a molecule (cf Figure 1). At room temperature (296 K) they are observed at 35.670 MHz as an almost single line. The temperature dependence of the NQR frequencies are shown in Figure 3. The first-order phase transition at T_c = 399 K found by DSC measurements [1] was clearly detected as a discontinuity of the temperature dependence of the NQR frequencies. The same number of the NQR lines were observed at high-temperature phase (HTP) as well. A large thermal hysteresis of ca. 30 K was observed in the temperature dependence of the NQR frequencies with increasing and decreasing temperature. It is rather surprising that the difference in frequency (ca. 100 kHz) of the two NQR lines in the HTP is larger than that (ca. 10 kHz) of the low-temperature phase (LTP), since there are only a small number of examples of symmetry lowering upon heating. Recently, however, by symmetry adapted distortion mode analysis, the structure of HTP was shown to belong to the monoclinic polar space group *Pc*, while the LTP belongs to the orthorhombic polar space group *Pca*2$_1$ with higher symmetry [5]. The symmetry-lowering transition on warming from orthorhombic *Pca*2$_1$ to monoclinic *Pc* seems to be consistent with the increase of the difference in frequency of the two NQR lines in the phase transition from LTP to HTP.
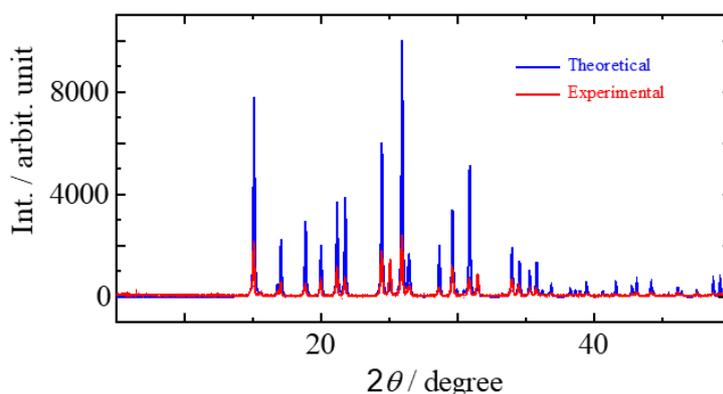
Figure 2. Powder X-ray diffraction of DC-MBI crystal taken at room temperature using Cu Kα radiation. Theoretical pattern was calculated for *Pca*2_1, a = 14.238(3), b = 5.6866(12), c = 10.398(2) Å, Z = 4 at 295 K [1].
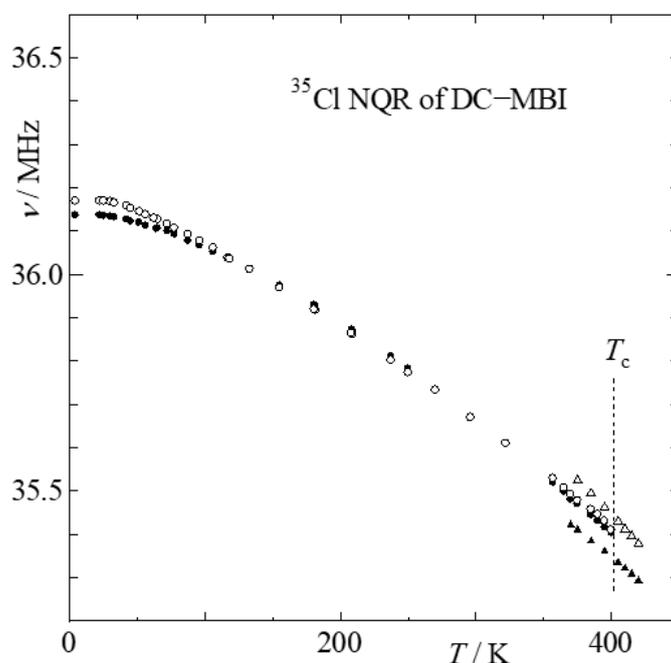
Figure 3. Temperature dependence of ^{35}Cl NQR frequencies of DC-MBI. The phase transition temperature T_c observed with increasing temperature is indicated by a vertical line. The two frequencies in LTP and HTP are shown by solid and open circles, and solid and open triangles, respectively.

Figure 4 shows the temperature dependence of ^{35}Cl NQR spin-lattice relaxation time T_{1Q} in LTP. In Figure 4 (right), the ln (T_{1Q}/s) is plotted against ln (T/K). The temperature dependence can be explained by the power law of $T_{1Q}^{-1} = a\,T^n$ with n = 2.05, a = 2.37 × 10^{-4} s^{-1} K^{-n} depicted by the solid line in Figure 4 (right). Therefore, the NQR relaxation seems to be governed by the lattice vibration [6]. In Figure 4 (left), the T_{1Q}/s is plotted in logarithmic scale against 10^3 K/T. In this type of plot, a possible quantum relaxation effect is expected to appear as for T_{1Q} to approach a constant value with increasing 10^3 K/T. Even with cooling down to ca. 25 K, the T_{1Q} showed no sign of approaching a constant value at low temperatures. In the present study, no sign of domain-wall motion by quantum tunneling was detected. The T_{1Q} measured in HTP showed similar values as in LTP and no appreciable change was observed at the first-order phase transition.
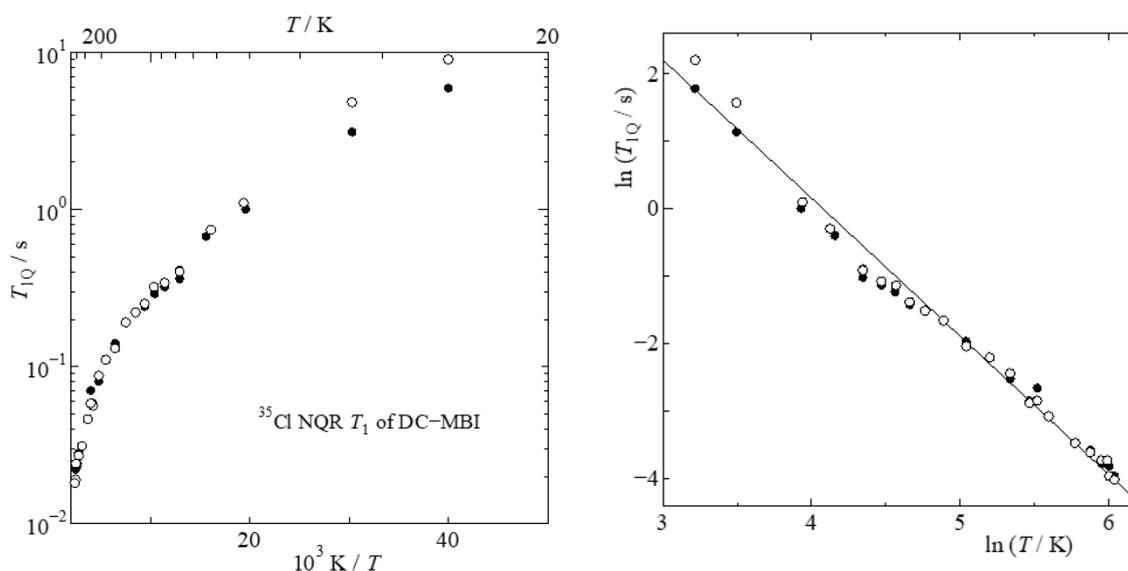
Figure 4. Temperature dependence of ^{35}Cl NQR spin-lattice relaxation time T_{1Q} of DC-MBI. Data shown by solid and open circles are of the frequencies shown by the same symbols in Figure 3, respectively.

In order to check the possibility of detecting a protonic motion in the N-H...N hydrogen bonds, temperature dependence of ^{1}H NMR T_1 was also measured. The results are shown in Figure 5, in which T_1 is plotted in ordinate using logarithmic scale against the reciprocal temperature 10^3 K/T. An asymmetric T_1 minimum of *ca.* 1 s was observed at *ca.* 35 K. This T_1 minimum can be ascribed to the methyl group reorientation. We measure the averaged relaxation rate T_1^{-1} which consists of the contribution from methyl proton T_{1,CH_3}^{-1} and that from the other protons $T_{1,\text{other}}^{-1}$. Considering the number of protons in the DC-MBI molecule and that all molecules are crystallographically equivalent, the weighted average will be given by (1) since the number of methyl proton and that of the other protons in the molecule are both equal to three.

$$T_1^{-1} \;=\; \frac{1}{2}\,T_{1,\text{CH}_3}^{-1} \;+\; \frac{1}{2}\,T_{1,\text{other}}^{-1} \tag{1}$$

At low temperatures below 100 K, in which the molecular motion as a whole molecule is expected to be frozen, the contribution from methyl group reorientation will dominate the relaxation. Then, the following can be assumed.

$$T_1^{-1} \;=\; \frac{1}{2}\,T_{1,\text{CH}_3}^{-1} \tag{2}$$

Since the T_1 minimum due to the classical reorientation of the methyl group is estimated to be *ca.* 0.026 s at 45.08 MHz assuming the second moment reduction of intramethyl dipolar interaction by C_3 reorientation of the methyl group is equal to 1.15×10^{10} Hz^2 (16 G^2) [7], the T_1 minimum of *ca.* 0.052 s is expected in our compound. The observed T_1 minimum value of ca. 1 s is about twentyfold greater than the estimated value. This fact as well as the asymmetric T_1 minimum curve suggest the quantum nature of the methyl group reorientation [8]. Anyway, any protonic motion in the N-H...N hydrogen bonds was hardly observed in the temperature dependence of ^{1}H T_1 due to the dominant contribution from the methyl group reorientation. Besides the domain-wall motion, proton jump between the bistable potential minima localized in the N-H...N hydrogen bonds may also be possible at higher temperatures above room temperature. However, there exists no sign of such motional excitation in the temperature dependence. The potential barrier for a proton to jump between the bistable potential minima is expected to be high because of the long N . . . N distance of 2.98 Å [1].
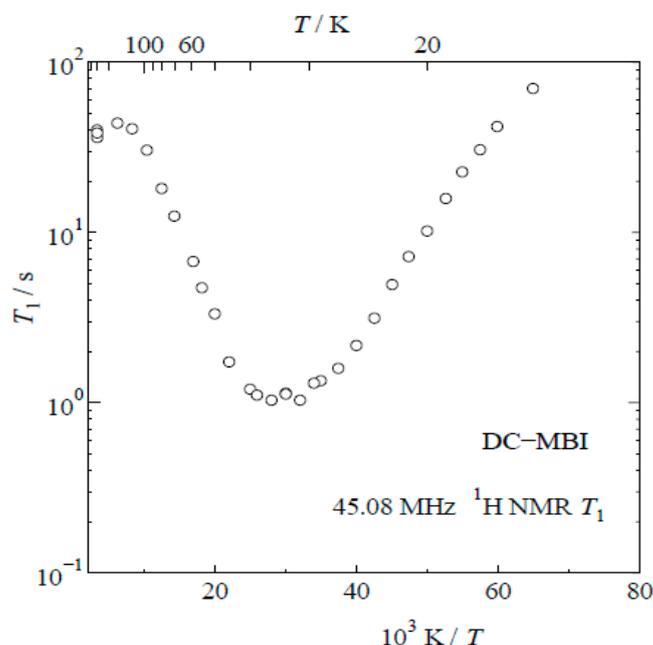
Figure 5. Temperature dependence of ^{1}H NMR spin-lattice relaxation time T_1 of DC-MBI.

4. Conclusions

Molecular ferroelectric 5,6-dichloro-2-methylbenzimidazole (DC-MBI) undergoes the first-order phase transition at around 400 K accompanied with a large thermal hysteresis of ca. 30 K. [35]Cl NQR frequencies of the two crystallographically nonequivalent chlorine atoms in a DC-MBI molecule were determined both in the low- and high-temperature phases. The difference in frequency of the two chlorine NQR lines increased from ca. 10 kHz to ca. 100 kHz through the phase transition on warming. This is consistent with the recently reported symmetry-lowering of crystal structure on warming through the phase transition temperature. Attempting to detect a possible quantum dynamics of domain walls in molecular ferroelectrics, [35]Cl NQR and ^{1}H NMR spin-lattice relaxation times were measured as a function of temperature. The temperature dependence of the NQR spin-lattice relaxation time was explained by the power law of $T_{1Q}^{-1} = a\,T^n$ with $n = 2.05$, $a = 2.37 \times 10^{-4}$ s^{-1} K^{-n}. No sign of domain-wall motion by quantum tunneling was detected in the NQR as well as ^{1}H NMR spin-lattice relaxation.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Horiuchi, S.; Kagawa, F.; Hatahara, K.; Kobayashi, K.; Kumai, R.; Murakami, Y.; Tokura, Y. Above-Room-Temperature Ferroelectricity and Antiferroelectrcicity in Benzimidazoles. *Nat. Commun.* **2012**, *3*, 1308. [CrossRef] [PubMed]
2. Kagawa, F.; Minami, N.; Horiuchi, S.; Tokura, Y. Athermal Domain-Wall Creep near a Ferroelectric Quantum Critical Point. *Nat. Commun.* **2016**, *7*, 10675. [CrossRef]
3. Minami, N.; Kagawa, F.; Horiuchi, S.; Tokura, Y. Quantum Relaxation Dynamics of Domain Walls in Imidazole Hydrogen Bonded Ferroelectrics. In Proceedings of the Abstract of the Physical Society of Japan 2013 Autumn Meeting, 27pKA-4, Tokushima, 25–28 September 2013. [CrossRef]
4. Brooke, J.; Rosenbaum, T.F.; Aeppll, G. Tunable Quantum Tunneling of Magnetic Domain Walls. *Nature* **2001**, *413*, 610–613. [CrossRef] [PubMed]

5. Liu, H.; Zhang, W.; Halasyamani, P.S.; Stokes, H.T.; Campbell, B.J.; Evans, J.S.O.; Evans, I.R. Understanding the Behavior of the Above-Room-Temperature Molecular Ferroelectric 5,6-Dichloro-2-methylbenzimidazole Using Symmetry Adapted Distortion Mode Analysis. *J. Am. Chem. Soc.* **2018**, *140*, 13441–13448. [CrossRef] [PubMed]

6. Chihara, H.; Nakamura, N. Study of Molecular Motion by Nuclear Quadrupole Resonance and Relaxation. In *Advances in Nuclear Quadrupole Resonance*; Smith, J.A.S., Ed.; Heyden: London, UK, 1980; Volume 4, pp. 1–69.

7. Asaji, T.; Ashitomi, K. Phase Transition and Cationic Motion in a Metal-Organic Perovskite, Dimethylammonium Zinc Formate [$(CH_3)_2NH_2$] [$Zn(HCOO)_3$]. *J. Phys. Chem. C* **2013**, *117*, 10185–10190. [CrossRef]

8. Haupt, J. Einfluß von Quanteneffekten der Methylgruppenrotation auf die Kernrelaxation in Festkörpern. *Z. Nat. A* **1971**, *26*, 1578–1589. [CrossRef]